The Blackett Memorial Lecture, 1991: Chemical Insights into High-Temperature Superconductors

C. N. R. Rao

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The Blackett Memorial Lecture, 1991

Chemical insights into high-temperature superconductors

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Contents

The high-temperature superconductors are complex oxides, generally containing two-dimensional CuO_2 sheets. Various families of the cuprate superconductors are described, paying special attention to aspects related to oxygen stoichiometry, phase stability, synthesis and chemical manipulation of charge carriers. Other aspects discussed are chemical applications of cuprates, possibly as gas sensors and copper-free oxide superconductors. All but the substituted Nd and Pr cuprates are hole-superconductors. Several families of cuprates show a nearly constant n_h at maximum T_c. Besides this universality, the cuprates exhibit a number of striking common features. Based on Cu(2p) photoemission studies, it is found that the Cu–O charge-transfer energy, Δ, and the Cu(3d)–O(2p) hybridization strength, t_{pd}, are key factors in the superconductivity of cuprates. The relative intensity of the satellite in the Cu(2p) core-level spectra, the polarizability of the CuO_2 sheets as well as the hole concentration are related to Δ/t_{pd}. These chemical bonding factors have to be explicitly taken into account in any model for superconductivity of the cuprates.

1. Introduction

I am delighted that I have been asked to deliver the Blackett Memorial Lecture this year. Professor Blackett was a man of many parts and was keenly interested in India,

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especially with regard to the policy for science and development. I have been myself involved in planning science and technology for development in the past few years and have greatly appreciated the concerns of Professor Blackett. Although I am not certain whether Professor Blackett would have predicted the science and technology scenario prevalent today, I feel that he would have been amused by a chemist from India talking about recent developments in warm superconductors. I have chosen this topic not only to demonstrate how chemists have much to do in this frontline area of condensed matter science, but also to show how certain classes of transition metal oxides – on which I have been working for many years (Rao & Subbarao 1970; Rao 1989) in a corner of the globe – have become so prominent because of high-temperature superconductivity. This area is no longer the one I pursued years ago out of curiosity, but one which has become so competitive that it is foolhardy to try to read all the literature. It has been really an exciting experience to witness this area develop explosively in so short a time.

Metal oxides themselves are not new to superconductivity. Superconducting transition temperatures of around 13 K were obtained some years ago in $Li_{1+x}Ti_{2-x}O_4$ (Johnston *et al.* 1973) and $BaBi_{1-x}PbO_3$ (Sleight *et al.* 1975). The discovery of superconductivity in the La–Ba–Cu–O system (Bednordz & Müller 1986) pushed the upper limit of the transition temperature from a stagnant value of 23 K to around 30 K and initiated an unprecedented pace of search for high-temperature superconductivity. The superconducting phase in the La–Ba–Cu–O system had the quasi two-dimensional K_2NiF_4 structure containing a perovskite layer, the parent compound being La_2CuO_4. I may recall here that my own interest in the structure and properties of this class of transition metal oxides goes back to several years (Ganguly & Rao 1973, 1984). When superconductivity above the liquid nitrogen temperature was reported in the Y–Ba–Cu–O system in early 1987 (Wu *et al.* 1987), we independently identified the phase responsible for superconductivity to be $YBa_2Cu_3O_7$ with a defect perovskite structure (Rao *et al.* 1987). We have since worked on several other families of superconducting cuprates, all containing perovskite layers, the highest T_c till to date being 125 K. High-temperature superconductivity is not restricted to cuprates alone, but what is interesting is that all the high T_c materials discovered up to now are metal oxides. It is not entirely unlikely that the ability of the metal–oxygen bond to traverse the entire range from the extreme ionic limit to the highly covalent limit is related to this feature. We cannot forget that transition metal oxides are versatile materials (Rao & Subbarao 1970; Goodenough 1971; Rao 1989) showing metallic behaviour at one end (e.g. ReO_3, $LaNiO_3$) and insulating behaviour at the other (e.g. $BaTiO_3$); then, we have oxides exhibiting metal–insulator transitions (e.g. V_2O_3, $LaNi_{1-x}Mn_xO_3$, $La_{1-x}Sr_xCoO_3$). Oxides can be ferromagnetic (e.g. $La_{0.5}Sr_{0.5}MnO_3$) or antiferromagnetic (e.g. $LaCrO_3$). Metal oxides exhibit interesting electronic properties arising from valence ordering (e.g. Fe_3O_4), charge-density-wave transitions (e.g. Na_xWO_3) and defect ordering (e.g. $Ca_2Fe_2O_5$). Properties of transition metal oxides depend on the dimensionality as well. Thus two-dimensional oxides do not exhibit ferromagnetism or real metallicity (Rao *et al.* 1988). The various cuprate families exhibiting superconductivity possess two-dimensional CuO_2 sheets just like La_2CuO_4.

I present here some of the highlights of the structure–property relations in the various families of high T_c cuprates and illustrate how chemistry plays a major role in the development of such important materials and how solid state chemistry constitutes a fascinating and important branch of chemical science in its own right.

Chemical literature on high-temperature superconductors has become voluminous and I shall therefore cite only some of the very recent references, primarily those based on the work carried out in my laboratory. The earlier results have been adequately covered in many reviews and conference reports (Cava 1990; Goodenough & Manthiram 1990; Joshi *et al.* 1990; Kitazawa & Ishiguro 1989; Nelson *et al.* 1987; Ramakrishnan & Rao 1989; Rao 1988*a*, *b*; Rao & Raveau 1989; Sleight 1988). I shall attempt to point out the important commonalities among the various families of cuprate superconductors and examine such chemical factors as stoichiometry, oxygen disorder, oxidation states, phase stability and chemical manipulation of charge carriers as well as the crucial role of chemical bonding in understanding the phenomenon of high-temperature superconductivity. I shall also briefly touch upon certain synthetic aspects and possible chemical applications of these materials.

2. Cuprate families

The first family of high-temperature oxide superconductors are derived from La_2CuO_4 possessing the K_2NiF_4 structure (figure 1). Stoichiometric La_2CuO_4 is an antiferromagnetic insulator which when doped with holes (by formally creating trivalent Cu species through the substitution of La^{3+} by divalent ions such as Sr^{2+} or by incorporating excess oxygen) becomes superconducting. While La_2CuO_4 is orthorhombic at 300 K and becomes tetragonal at higher temperatures, super-conducting $La_{2-x}M_xCuO_4$ ($x \approx 0.2$ when $M = Sr$) is tetragonal at 300 K and becomes orthorhombic around 180 K, well above the superconducting transition temperature (*ca.* 35 K). Accordingly, the Cu–O–Cu angle in the superconducting oxides of K_2NiF_4 structure are slightly bent (less than 180°) causing a buckling of the Cu–O sheets. In figure 2, the phase diagram of $La_{2-x}Sr_xCuO_4$ is shown to indicate the narrow range of the antiferromagnetic phase and the maximum in T_c at a specific value of x where the hole concentration is also a maximum (Torrance *et al.* 1988). Some doubt has been raised as to whether the maximum T_c at $x \approx 0.2$ exhibited by $La_{2-x}Sr_xCuO_4$ is due to the presence of inhomogeneities in the compositions other than the one showing maximum T_c. This seems unlikely; as we will show later, the T_c maximum occurs at an optimal hole concentration in all the families of cuprate superconductors (Rao *et al.* 1991*a*). In oxygen-excess $La_2CuO_{4+\delta}$, however, separation into superconducting and antiferromagnetic phases seems to occur (Chaillout *et al.* 1990; Jorgensen *et al.* 1988).

The La^{3+} ion in $La_{2-x}M_xCuO_4$ can be substituted to some extent by Pr^{3+} and other rare earth ions without losing superconductivity. It is to be noted that Pr_2CuO_4 and Nd_2CuO_4 themselves possess the so-called T′-structure with square-planar CuO_4 units unlike the T-structure of La_2CuO_4. The T and T′ cuprates form solid solutions over a reasonable range of compositions (Goodenough & Manthiram 1990; Singh *et al.* 1982).

The next homologue of the $La_{2-x}Sr_xCuO_4$ family containing two CuO_2 sheets had earlier been reported to be an insulator. However, recently Cava *et al.* (1990*a*) have synthesized $(La,Sr)_2CaCu_2O_6$ under a high oxygen pressure and found it to be superconducting with a T_c of 60 K. This removes the discomfort one had related to the absence of superconductivity in the two-layer cuprate of this family and also underscores the importance of oxygen stoichiometry. Vijayaraghavan has recently synthesized analogous double-layer compounds of the general formula $LaSrLnCu_2O_6$ ($Ln = Nd$, Gd or Y) in my laboratory.

Figure 2

Figure 1

- • Cu
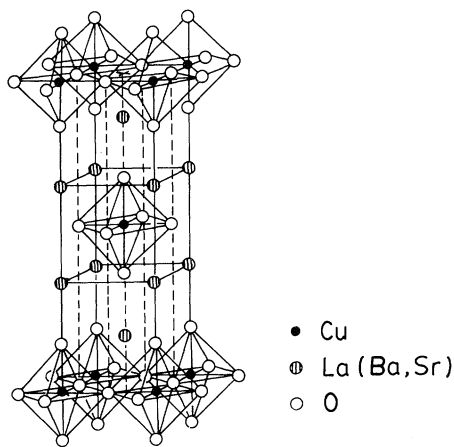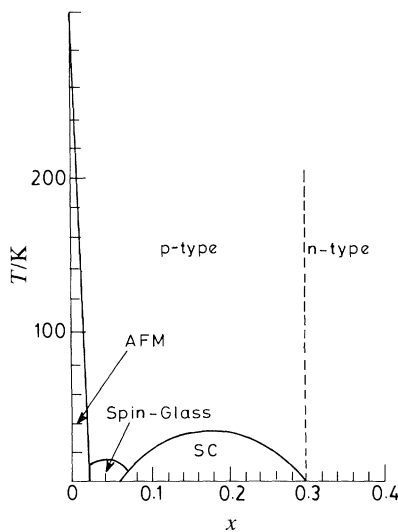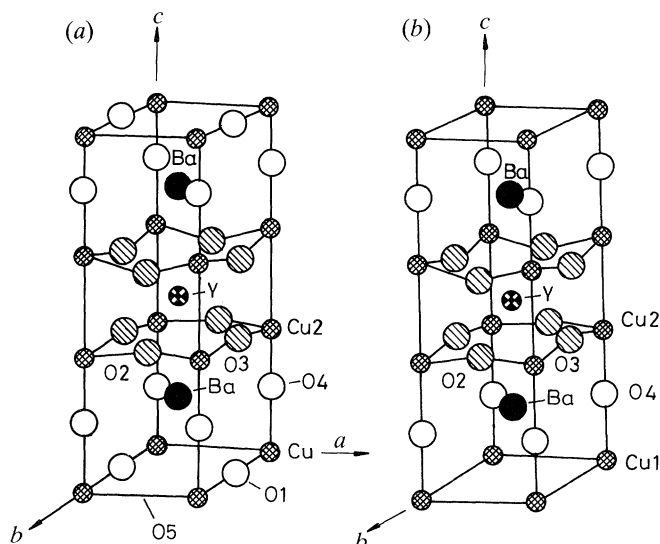- ◍ La (Ba,Sr)
- ○ O

Figure 1. Structure of $La_{2-x}Sr_xCuO_4$.

Figure 2. Phase diagram of hole-doped $La_{2-x}Sr_xCuO_4$.

Figure 3. Structures of (a) $YBa_2Cu_3O_7$ and (b) $YBa_2Cu_3O_6$.

$YBa_2Cu_3O_{7-\delta}$ and the other 123 cuprates of the general formula $LnBa_2Cu_3O_7$ (Ln is a rare earth other than Ce, Pr and Tb) show superconductivity with a T_c of *ca.* 90 K in the near stoichiometric compositions (not more than 0.2). These compounds have an orthorhombic structure. The structure as well as the superconductivity are sensitive to oxygen stoichiometry. Stoichiometric 123 cuprates contain Cu–O chains along the *b*-axis in addition to the CuO_2 sheets (figure 3). When the Cu–O chains are fully depleted of oxygen, we get the non-superconducting, tetragonal $YBa_2Cu_3O_6$.
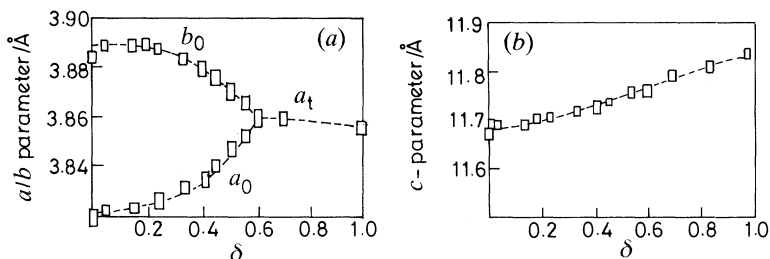
Figure 4. Variation of the lattice parameters of $YBa_2Cu_3O_{7-\delta}$ with δ.
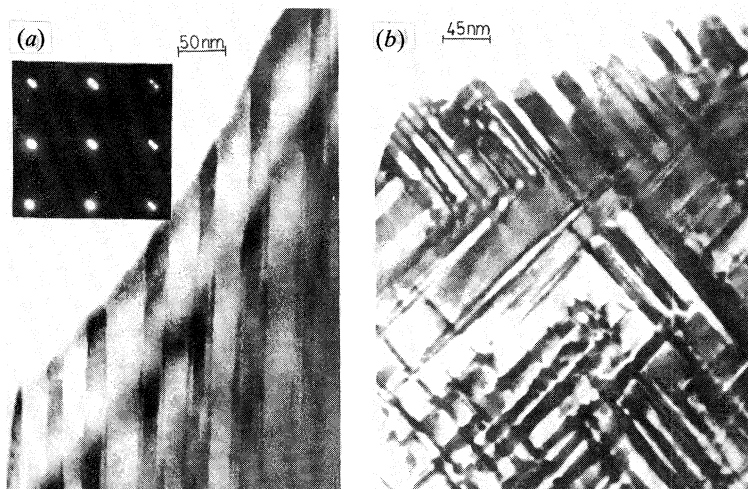

Figure 5. (*a*) Bright field electron microscopic images of twins in $YBa_2Cu_3O_7$. The splitting of the {110} Brugg spots is clearly seen in SAED pattern given in the inset. (*b*) 90° twins in $YBa_2Cu_3O_7$.

The variation of the unit cell parameters of $YBa_2Cu_3O_{7-\delta}$ with the oxygen stoichiometry is shown in figure 4 to illustrate how the orthorhombic structure gives way to the tetragonal structure around $\delta \approx 0.6$. All the $LnBa_2Cu_3O_7$ compounds undergo the orthorhombic tetragonal transition, the temperature of the transition depending on the Ln ion (Y = 970 K, La = 590 K). The orthorhombic phases show extensive twinning with a rotation of the a and b axes across the twin boundary. In figure 5 we show typical twins recorded by us in early March 1987. The twinning has no direct bearing on superconductivity; accordingly non-superconducting $PrBa_2Cu_3O_7$ shows twinning because of the orthorhombic structure.

The variation of T_c with δ in $YBa_2Cu_3O_{7-\delta}$ is shown in figure 6. We see that T_c is nearly constant (*ca.* 90 K) upto $\delta = 0.2$ and then drops sharply showing a sort of a plateau around 60 K for $\delta = 0.3$–0.4; the T_c value reaches 45 K when $\delta = 0.5$. The formal valence of Cu in the sheets also shows a plateau in the 60 K region as shown in figure 6 (Cava *et al.* 1990*b*).

$YBa_2Cu_3O_{6.5}$ ($\delta = 0.5$) is a oxygen vacancy-ordered structure with fully oxidized Cu–O chains (O_7 units) alternating empty chain (O_6 units) as shown in figure 7. In $YBa_2Cu_3O_7$ and related 123 compounds, the orthorhombic c parameter is exactly equal to $3b$ (figure 8). $YBa_2Cu_3O_{6.75}$ also seems to have a vacancy-ordered structure (figure 7), but compositions with δ between 0.3 and 0.4 ($T_c \approx 60$ K) show no such
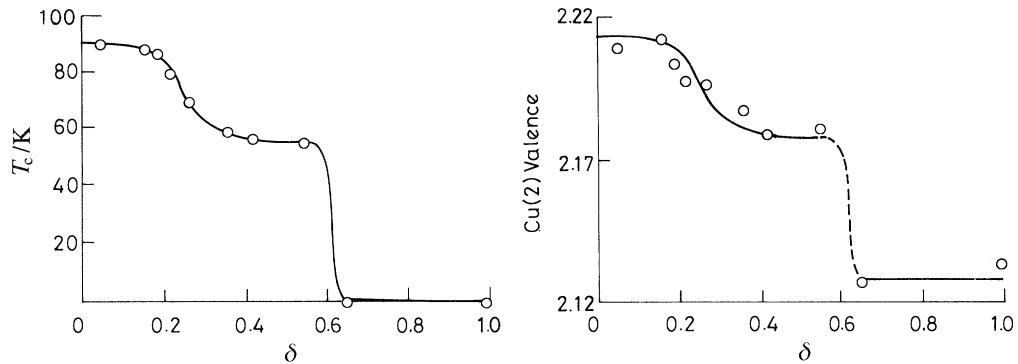
Figure 6. Variation of the T_c and in-plane Cu(2) valence of $YBa_2Cu_3O_{7-\delta}$ with δ (From Cava *et al.* 1990b).
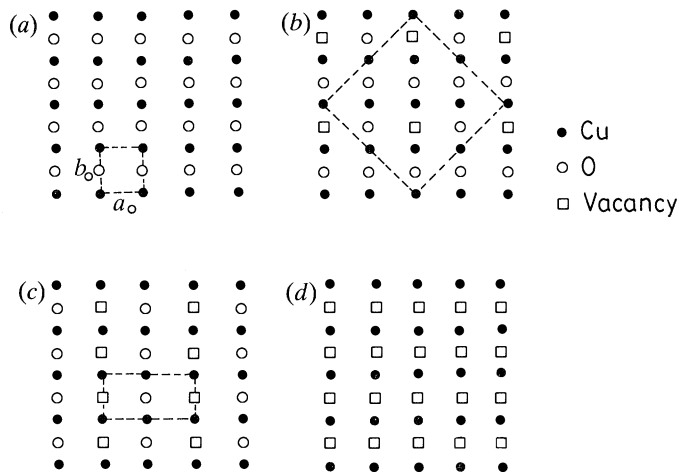

Figure 7. Structure of the basal (ab) plane of $YBa_2Cu_3O_{7-\delta}$: (a) $\delta = 0$, (b) $\delta = 0.25$, (c) $\delta = 0.5$, (d) $\delta = 1.0$. (From Rao *et al.* 1990d.)

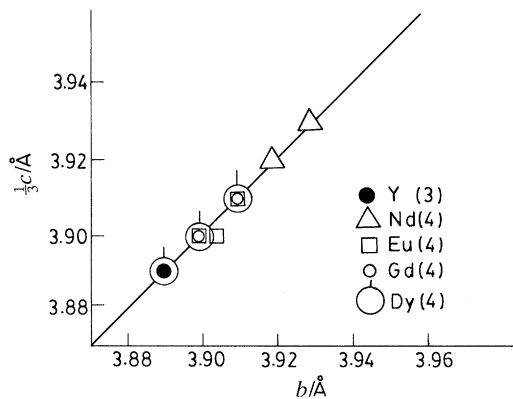Figure 8. Relation between the c and b parameters in orthorhombic $LnBa_2Cu_3O_{7-\delta}$ (Ln = rare earth or Y, $\delta < 0.2$). (From Rao *et al.* 1990d.)

ordering. It has indeed been shown that this composition range is metastable, disproportionating to orthorhombic and tetragonal phases on annealing at low temperatures of the order of 470 K (Rao *et al.* 1990*a*). Thus, on annealing $YBa_2Cu_3O_{6.7}$ at 470 K for a few hours, the X-ray diffraction pattern changes drastically while the electron diffraction pattern shows considerable streaking. Every oxygen added in this δ range oxidizes Cu^+ in the chains without adding extra holes to the CuO_2 sheets, thereby giving rise to the T_c (as well as the Cu valence) plateau around 60 K (figure 6). It is noteworthy that tetragonal $YBa_2Cu_3O_{6.8}$ even though oxygen-rich and contains a fair proportion of Cu^{III} species, is not superconducting since the different Cu layers get connected three dimensionally through the presence of orthorhombic microdomains (Caignaert *et al.* 1990). In $YBa_2Cu_3O_{6.4}$, local oxygen ordering seems to increase the T_c from 0 to 20 K (Jorgensen *et al.* 1990).

The chemistry of $YBa_2Cu_3O_{7-\delta}$ is best understood starting with $YBa_2Cu_3O_6$ ($\delta = 1.0$) which is an antiferromagnetic insulator containing Cu^I ions in the chain. As oxygen diffuses into tetragonal $YBa_2Cu_3O_6$, the linear O–Cu^I–O units are progressively converted into square-planar CuO_4 that share corners to form chains (figure 3); when *ca.* 40% of the Cu–O chains are thus oxidized, we get the orthorhombic structure. Fully oxidized $YBa_2Cu_3O_7$ itself can be formally considered to be $YBa_2Cu_2^{II}Cu^{III}O_7$. Substitution chemistry of $YBa_2Cu_3O_{7-\delta}$ has been examined by several workers who have partly substituted Cu by Fe, Ni or Zn; such substitutions are generally unfavourable to superconductivity just as in the case of $La_{2-x}Sr_xCuO_4$. By substitution of Ba by La or Y by Ca in $YBa_2Cu_3O_7$, one changes the oxygen stoichiometry and also brings about a decrease or an increase in the carrier concentration (Manthiram & Goodenough 1989; Tokura *et al.* 1988). We should note here that only the holes in the CuO_2 sheets are pertinent to superconductivity. It is therefore necessary to subtract out the holes in the chains from the total hole concentration as given by n_h (plane) $= \frac{3}{2}$ (n_h total $- n_h$ chain) (Shafer & Penney 1990).

As mentioned earlier, $PrBa_2Cu_3O_7$ is not superconducting (Ganguli *et al.* 1989*c*). This was first considered to be due to the presence of a small proportion of the Pr ions in the $4+$ state. It now seems that this is not the case. It has been suggested that the presence of Pr (4f) levels in the vicinity of the Cu–O band could be responsible for the absence of superconductivity (Sarma *et al.* 1991). The recent observation (Norton *et al.* 1991) of superconductivity ($T_c \approx 43$ K) in films of $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$, however, suggests that absence of superconductivity in Pr cuprate $PrBa_2Cu_3O_7$ may be related to the small hole concentration. This aspect needs to be examined further.

Basically, $YBa_2Cu_3O_7$ is not thermodynamically stable. The more stable $YBa_2Cu_4O_8$ containing two Cu–O chains (figure 9) formed by CuO_4 units sharing edges has been prepared. This cuprate has a T_c of 80 K. Other rare earth analogues of the general formula $LnBa_2Cu_4O_8$ are also known. Although the so-called 124 compounds were first prepared under high oxygen pressures (Karpinski *et al.* 1988), they can be prepared under ambient conditions (Cava *et al.* 1989; Liu *et al.* 1990; Rao *et al.* 1990*d*). Superconducting 247 compounds of the general formula $Ln_2Ba_4Cu_7O_{15}$ with a T_c of *ca.* 90 K have been characterized. The structure of these compounds may be considered to be composed of an 1:1 ordered intergrowth of $LnBa_2Cu_3O_7$ and $LnBa_2Cu_4O_8$ (figure 9). Recall $LnBa_2Cu_3O_{6.5}$ is an 1:1 intergrowth of $LnBa_2Cu_3O_7$ and $LnBa_2Cu_3O_6$. The 247 as well as the 124 cuprates on thermal decomposition give 123 throwing out excess CuO. Effects of temperature and pressure on the structures of the 124 and 247 cuprates have been examined in detail
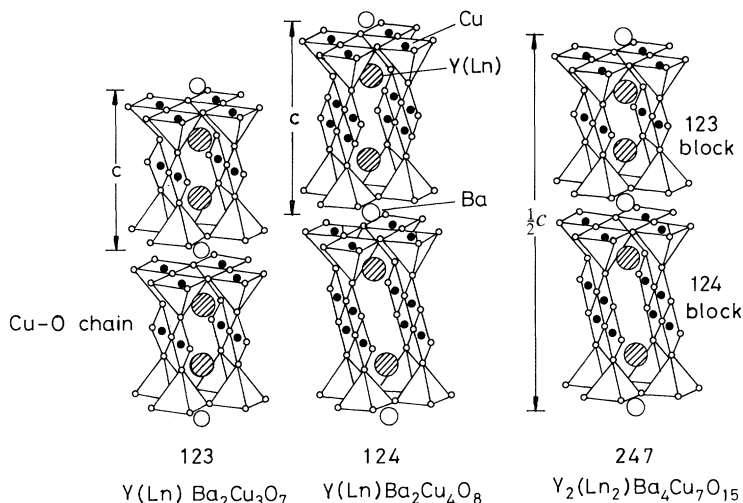
Figure 9. Comparison of the structures of 123, 124 and 247 cuprates. Note the presence of two chains in 124.
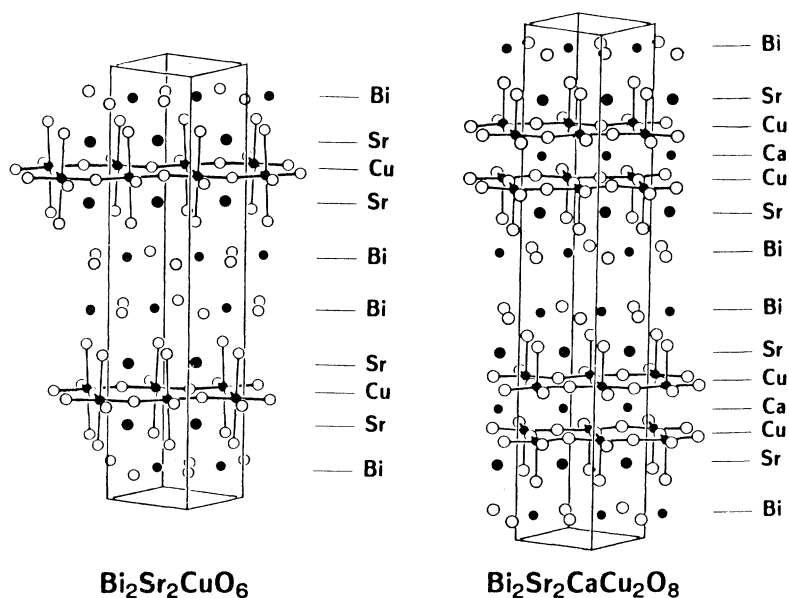
Figure 10. Structures of Bi cuprates. (From Torardi *et al*. 1989.)

by Hewat *et al*. (1990). Properties of the 124 cuprate have been reviewed by Miyatake *et al*. (1990).

Bismuth cuprates of the general formula $Bi_2(Ca,Sr)_{n+1}Cu_nO_{2n+4}$ possessing an orthorhombic structure and containing two rock-salt type layers of BiO constitute an important family of superconductors, with the $n = 2$ and the $n = 3$ members showing T_cs of 90 K and 110 K respectively (figure 10). The $n = 1$ member of the formula $Bi_{2+x}Sr_{2-x}CuO_6$ (without Ca) shows a maximum T_c of around 20 K. The $n = 1$ member containing calcium has been reported, but it does not appear to be

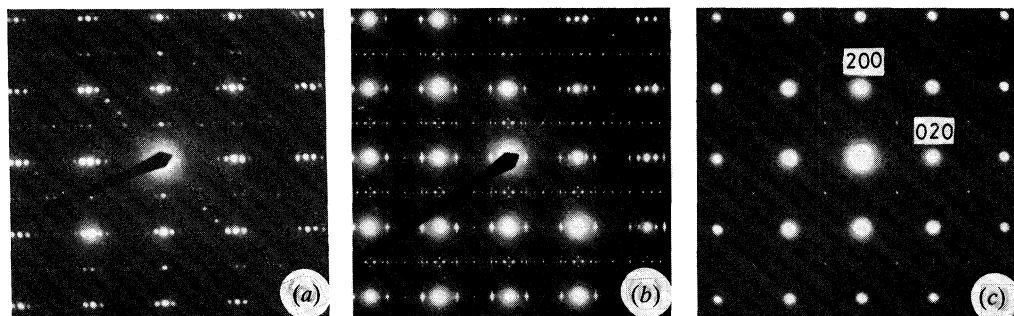Figure 11. Electron diffraction patterns showing (*a*) superlattice modulation in superconducting $Bi_2CaSr_2Cu_2O_8$ recorded along the (001) direction, (*b*) superlattice modulation in non-superconducting $Bi_2YSr_2Cu_2O_8$, and (*c*) absence of superlattice modulation in superconducting $BiPbSr_2Y_{0.5}Ca_{0.5}Cu_2O_8$.

superconducting. One of the difficulties with the bismuth cuprates is that it is difficult to make them absolutely monophasic because of the presence of disordered intergrowths of different sequences. A unique feature of the bismuth cuprate superconductors is that they exhibit 4*b*-type superlattice modulation along the *b*-direction (figure 11) due to the insertion of extra oxygens in the BiO layers (LePage *et al.* 1989). It was first thought that superconductivity in these compounds had some relation to the superlattice modulation. However, it was possible to prepare compounds of the type $Bi_2Sr_2LnCu_2O_8$ (Ln = Y or rare earth) which are not superconducting but exhibited superlattice modulation (figure 11) of the 4*b* or the 8*b* type (Rao *et al.* 1990*b*). Similarly, non-superconducting modulation-free oxides of the type $BiPbSr_2MO_y$ (M = Mn, Fe or Co) have been prepared (Tarascon *et al.* 1990). Recently, we have been able to prepare two series of superconductors of the general formula $BiPbSr_{1+x}Ln_{1-x}CuO_6$ (maximum $T_c \approx 80$ K) both of which are modulation-free (Manivannan *et al.* 1991) as can be seen from figure 11. Since Pb in these cuprates is in the 2+ state, it helps to decrease the oxygen content in the BiO layers, thereby eliminating the modulation. In both these new series of superconductors, the hole concentration, n_h, varies with x and the T_c reaches a maximum value at an optimal value at n_h.

An interesting series of bismuth cuprates in terms of the variation of the T_c as well as the hole concentration with composition is provided by $Bi_2Sr_2Ca_{1-x}Ln_xCu_2O_8$ where Ln = Y or rare earth (Rao *et al.* 1990*b*). The electrical resistivity data show a metal–insulator transition in the normal state with change in x (figure 12). The T_c as well as the n_h show a maximum at a composition of $x = 0.25$ (figure 13). Note that when Ca is fully substituted by Ln, the material becomes a non-superconducting insulator. Hole concentration in these bismuth cuprates is readily determined by Fe^{II}–Fe^{III} redox titrations.

Thallium cuprates of the general formula $Tl_2Ca_{n-1}Ba_2Cu_nO_{2n+4}$ with two Tl–O layers possessing a tetragonal structure (figure 14) show superconductivity with T_cs of 80, 110, and 125 K when $n = 1$, 2, 3 respectively. The corresponding $TlCa_{n-1}Ba_2Cu_nO_y$ series of cuprates with only a single Tl–O layer are also tetragonal (figure 14) with T_cs of 90 and 115 K respectively for $n = 2$ and 3. Higher members of the thallium cuprate families with $n > 3$ have been prepared, but the maximum T_c is generally found for $n = 3$. The thallium cuprates also exhibit disordered intergrowths of different members in most of the preparations. Oxygen stoichiometry
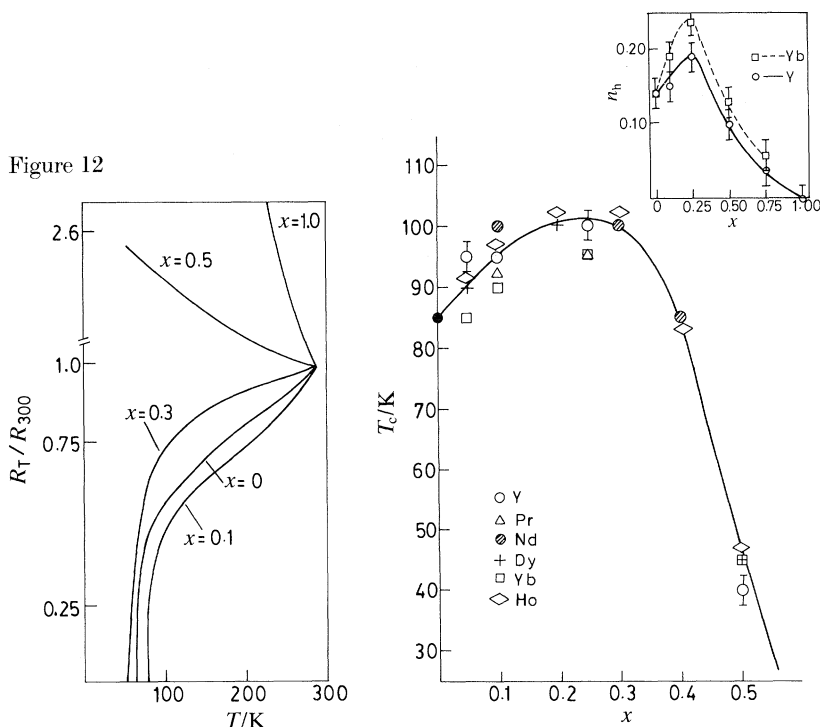
Figure 13

Figure 12. Resistivity data of superconducting $Bi_2Sr_2Ca_{1-x}Nd_xCu_2O_8$ showing the occurrence of a metal–insulator transition in the normal state. (From Rao *et al.* 1990*b*.)

Figure 13. Variation of T_c with composition in $Bi_2Ca_{1-x}Ln_xSr_2Cu_2O_{8+\delta}$. Inset shows variation of hole concentration n_h with DC. (From Rao *et al.* 1990*b*.)

plays an important role in the superconductivity of Tl cuprates as well. Thus hydrogen annealing of some of these materials increases the T_c (Maignan *et al.* 1990). A serious problem with these Tl cuprates is the difficulty in exactly determining the hole concentration. A method has been suggested recently in the literature (Manthiram *et al.* 1990), but it does not appear to be entirely satisfactory. A more reliable method has been developed by Gopalakrishnan and others in this laboratory by making use of a reducing agent (HBr) which selectively reacts with Cu^{III} giving Br_2 while thallium forms $TlBr_3$. The Tl cuprates are somewhat different from the corresponding bismuth cuprates although both Tl and Bi are essentially in the 3+ state. (Vijayakrishnan *et al.* 1990). The source of holes in the Tl cuprates is yet to be fully understood unlike in the bismuth cuprates (Goodenough & Manthiram 1990). It appears that one has to consider the presence of Tl vacancies as well as the possible overlap of the Tl(6s) band with the conduction band.

Although members of the Tl–Ca–Ba–Cu–O system of superconductors are readily prepared, the corresponding members of Tl–Ca–Sr–Cu–O cannot be prepared in pure form. It is, however, possible to prepare $Tl_{1-x}Pb_x(Ca,Sr)_{n+1}Cu_nO_y$ which are superconducting with the $n = 2$ member showing a T_c of 90 K and the $n = 3$ member a T_c of 120 K (Ganguli *et al.* 1988, 1989*b*; Subramanian *et al.* 1988). In these cuprates, Pb is in the 4+ state (Kulkarni *et al.* 1989), unlike in the Bi cuprates where it is in the 2+ state. A novel, analogous series of cuprates with the general formula,
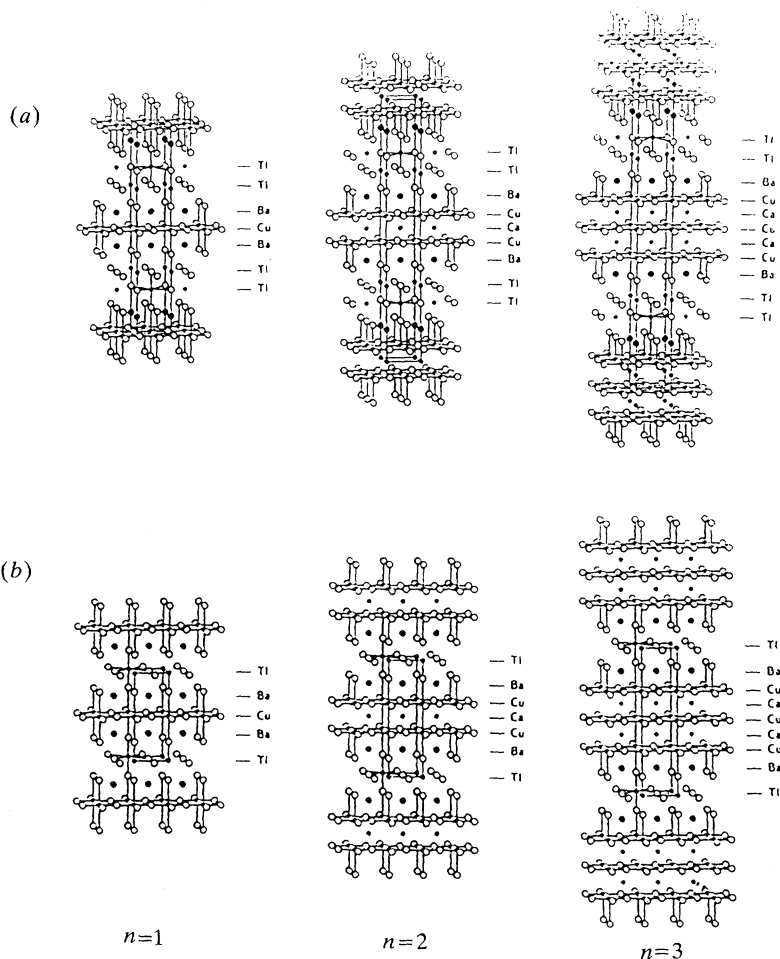
Figure 14. Structures of Tl cuprates of the type $Tl_mCa_{n-1}Ba_2Cu_nO_y$, where (*a*) $m = 1$ or (*b*) $m = 2$. (From Sleight *et al.* 1990.)

$TlCa_{1-x}Ln_xSr_2Cu_2O_y$ (Ln = Y or rare earth) has been prepared and characterized recently (Rao *et al.* 1989*a*, *c*). Here, Ca^{2+} is replaced by Ln^{3+} instead of Tl^{3+} by Pb^{4+} as in the earlier series. These cuprates also show a maximum T_c of 90 K. In figure 15 we show the electrical resistivity behaviour of a series of these cuprates; note the occurrence of the metal–insulator transition in the normal state as x is varied. The effect of substitution of Tl by Pb or of Ca by Ln is associated with the variation of the hole concentration. The interplay of chemical substitution with hole concentration can be nicely visualized in the $Tl_{1-y}Pb_yY_{1-x}Ca_xCu_2O_y$ system. This system may be considered as derived from the parent insulator $TlYSr_2Cu_2O_y$ wherein the substitution of Ca in place of Y increases the number of holes, while that of Pb in place of Tl does the opposite. Accordingly, T_c becomes maximum at a higher value of x (Ca concentration) as y (Pb concentration) increases as shown in figure 16. We notice that both T_c and the concentration of doped holes, x, reach a maximum at $y = 0.5$. The T_c goes up to 105 K by the chemical manipulation of hole concentration.

All the cuprate superconductors discussed hitherto contain Ca, Ba or/and rare earth. Recently, superconducting thallium cuprates not containing Ca, Ba or even a
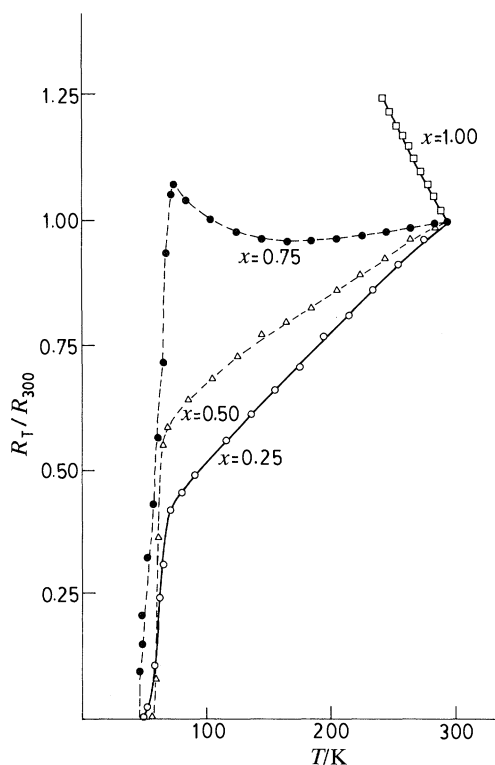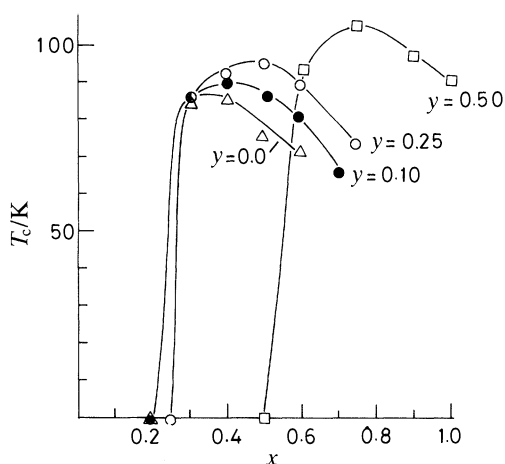
Figure 15

Figure 16

Figure 15. Resistivity data of superconducting $TlCa_{1-x}Nd_xSr_2Cu_2O_y$ showing composition-dependent metal–insulator transition in the normal state. (From Rao *et al.* 1989*c*.)

Figure 16. Variation of T_c with composition in $Tl_{1-y}Pb_yY_{1-x}Ca_xSr_2Cu_2O_y$. (Unpublished results of Vijayaraghavan, Grantscharova and Rao.)

rare earth have been characterized. Thus, in the series, $TlSr_{n+1-x}Ln_xCu_nO_{2n+3+\delta}$, the $n = 1$ and 2 members with T_cs of 40 and 90 K have been prepared (Ganguli *et al.* 1989*a*). Similarly, the $n = 3$ member in the series $(Tl,Pb)Sr_{n+1-x}Ln_xCu_nO_{2n+3}$ with a T_c of 60 K has been prepared though not in pure form (Manivannan *et al.* 1990). The $n = 1$ derivatives of these families may be considered to be derived from $TlSr_2CuO_5$. Substitution of La^{3+} for Sr^{2+} stabilizes the structure and reduces Cu^{III}, permitting superconductivity (Kovatcheva *et al.* 1991).

Lead cuprates of the general formula $Pb_2Sr_2(Ln,Ca)Cu_3O_8$ containing PbO layers and $O–Cu^I–O$ sticks (figure 17) with a T_c of about 60 K have been prepared (Cava *et al.* 1988*b*). In this system the average oxidation state of Cu is less than 2. The normal and superconducting state properties of $Pb_2Sr_2Y_{1-x}Ca_xCu_3O_{8+\delta}$ (note that the $x = 0.0$ composition is an insulator) have been examined in some detail (Koike *et al.* 1990). The superconducting lead cuprates have to be synthesized in an atmosphere deficient in oxygen (N_2 with 1 % O_2) to prevent oxidation of Cu and Pb. Analogous to the single Tl–O layer compounds, lead cuprates of the formula $(Pb,Cu)Sr_2(Y,Ca)Cu_2O_y$ are found to exhibit a T_c of 52 K (Maeda *et al.* 1990). Lower members of the Pb cuprate family of the type $(Pb,Cu)(SrLa)_2CuO_5$ (T_c of 34 K) have also been synthesized. Recently, a lead cuprate of the formula

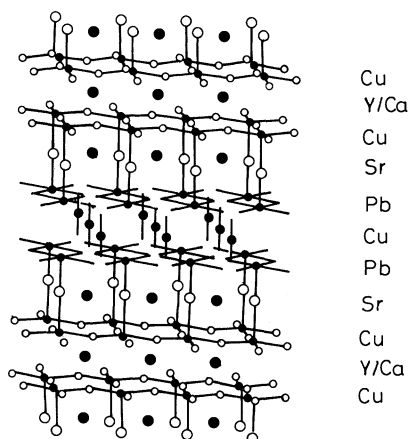Figure 17. Structure of $PbSr_2(Ca,Y)Cu_3O_8$ (after Sleight 1988).

$(Pb,Cu)(Eu,Ce)_2(Sr,Eu)_2Cu_2O_9$ containing a fluorite layer has been prepared with a T_c of 25 K (Maeda *et al.* 1990).

3. Nature of holes in the cuprate superconductors

All the cuprates described till now are hole superconductors. The nature of holes has been subject of considerable discussion (Chakraverty *et al.* 1988; Rao *et al.* 1989*b*; Sarma & Rao 1989). There has been no experimental evidence for the presence of Cu^{III} type species in the doped cuprates. Instead, there is considerable evidence from electron and X-ray spectroscopies for the presence of hybridized oxygen holes which can be represented as O^-. The detailed description of the holes in terms of the d and p characters has been investigated (Bianconi 1990). Essentially, the mobile holes in the cuprates are present in the in-plane π^* band which has O–2p character. The concentration of holes (in all but the Tl cuprates) are easily determined by iodometry or Fe^{II}–Fe^{III} titrations (Rao *et al.* 1991*a*; Shafer & Penney 1990). Since the Hall coefficients are temperature dependent, the chemical titration method becomes invaluable.

In figure 18, we show the variation of T_c with n_h (obtained by chemical titrations) in a number of cuprate families. We see that in all these families, the T_c goes through a maximum around the same hole concentration in the different series of cuprates containing the same number or CuO_2 sheets. Accordingly, $n_h \approx 0.2$ at the maximum T_c in all the cuprates containing two CuO_2 sheets. This universality is noteworthy. In figure 19 we show the variation of T_c in $Tl_{1-y}Pb_yY_{1-x}Ca_xSr_2Cu_2O_y$ against $(x-y)$ which is a direct measure of the hole concentration. We see that the maximum T_c (105 K) is found for $y = 0.25$ and 0.5 at a $(x-y)$ value of *ca.* 0.22. This value is close to the n_h value at maximum T_c in the other cuprates; the maximum T_c is lower when $(x-y)$ is larger as in the cases $y = 0.0$ and 0.1.

4. Electron-superconducting cuprates

Unlike the various cuprates discussed in §2 where the CuO_2 sheets could be doped with holes, Pr_2CuO_4 or Nd_2CuO_4 possessing the T' tetragonal structure (figure 20) can be doped with electrons by partly substituting Nd by Ce or Th or oxygen by fluorine

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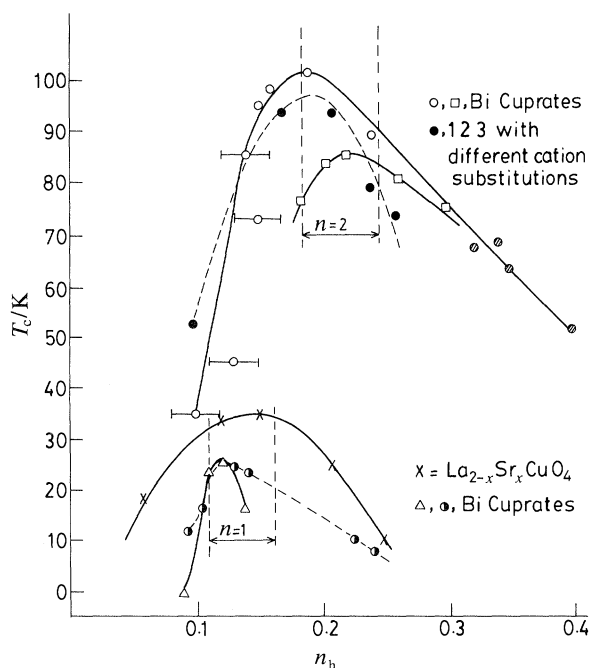
Figure 18

Figure 19
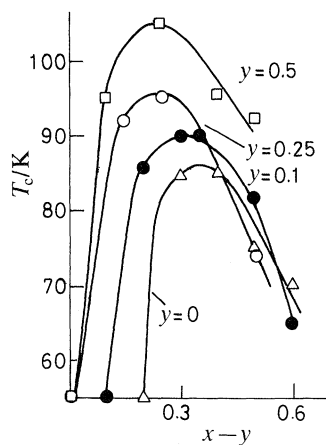
Figure 18. Variation of T_c with hole concentration in cuprates (from Rao *et al.* 1991 *a*).

Figure 19. Variation of T_c with effective hole concentration, $(x-y)$, in $Tl_{1-y}Pb_yY_{1-x}Ca_xSr_2CuO_y$.
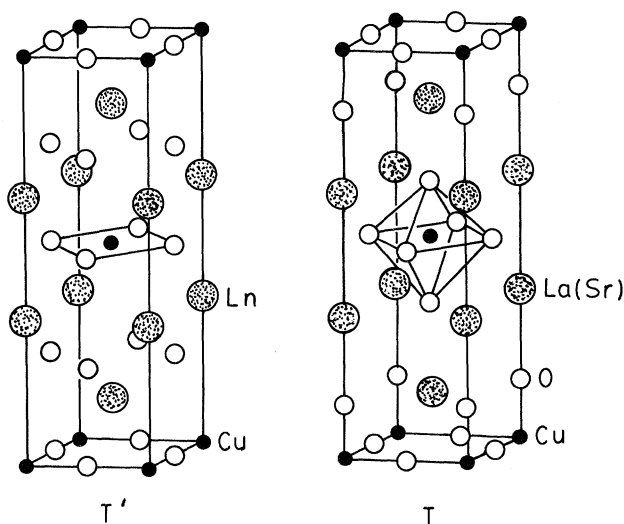
Figure 20. The T′ and T structure of cuprates (T, Ln = Nd, Pr, Ce).

(Maple 1990; Tokura *et al.* 1989 *b*). The maximum T_c that these compounds exhibit is around 25 K. Even though these cuprates are formally considered to be electron superconductors, the exact nature of the charge carriers is not fully certain. Some holes could also be present in such materials. In many ways, electron-super-

conducting cuprates are similar to the La_2CuO_4 family of hole superconductors. In $Nd_{2-x}Ce_xCuO_4$, it appears that the compositions are monophasic only for $x = 0.0$ and for the optimal x value where T_c is maximum (Lightfoot *et al.* 1990). Such inhomogeneity has been found in oxygen-excess Ln_2CuO_4 (Jorgensen *et al.* 1988). We do not have electron-superconducting oxides with T_cs comparable with those of the hole superconductors.

5. Synthetic aspects

In this section, I shall briefly present some preparative aspects of the cuprate superconductors based on the experience gained by us in the past four years. The cuprates are ordinarily made by the traditional ceramic method (mix, grind and heat), which involves thoroughly mixing the various oxides or/and carbonates (or any other salt) in the desired proportion and heating the mixture (preferably in pellet form) at a high temperature. The mixture is ground again after some time and reheated until the desired product is formed as indicated by X-ray diffraction. This method may not always yield the product with the desired structure purity or in oxygen stoichiometry. Variants of this method are often used. For example, decomposing a mixture of nitrates has been found to yield a better product in the case of the 123 compounds by some workers; some others prefer to use BaO_2 in place of $BaCO_3$ for the synthesis.

Coprecipitation and sol-gel methods are conveniently employed for the synthesis of 123 compounds and other cuprates. The sol-gel method provides a homogeneous dispersion of the various component metals when a solution containing the metal ions is transformed into a gel by adding an organic solvent such as a glycol or an alcohol often in the presence of other chemicals such as organic amines. The gel is then decomposed at relatively low temperatures to obtain the desired oxide, generally in fine particulate form. Materials prepared by such low-temperature methods may need to be annealed or heated under suitable conditions to obtain the desired oxygen stoichiometry as well as the characteristic high T_c. 124 cuprates, lead cuprates and bismuth cuprates have all been made by this method; the first two are particularly difficult to make by the ceramic method.

One of the problems with the bismuth cuprates is the difficulty in obtaining phasic purity (minimizing the intergrowth of the different layered phases). The glass or the melt route has been used to obtain better samples. The method involves preparing a glass by quenching the melt; the glass is then crystallized by heating it above the crystallization temperature. Thallium cuprates are best prepared in sealed tubes (gold or silver). Heating Tl_2O_3 with a matrix of the other oxides (already heated to 1100–1200 K) in a sealed tube is preferred by some workers. It is important that thallium cuprates are not prepared in open furnaces since Tl_2O_3 which readily sublimes is highly toxic. To obtain superconducting compositions corresponding to a particular copper content (number of CuO_2 sheets) by the ceramic method, one often has to start with various arbitrary compositions especially in the case of the Tl cuprates. The real composition of a bismuth or a thallium cuprate superconductor is not likely to be anywhere near the starting composition. The actual composition can be determined by analytical electron microscopy and other methods.

Heating oxidic materials under high oxygen pressures or in flowing oxygen often becomes necessary to attain the desired oxygen stoichiometry. Thus, La_2CuO_4 and $La_2Ca_{1-x}Sr_2Cu_2O_6$ heated under high oxygen pressure become superconducting with T_cs of 40 and 60 K respectively. In the case of the 123 compounds, one of the

problems is that it loses oxygen easily. It therefore becomes necessary to heat the material in an oxygen atmosphere at an appropriate temperature below the orthorhombic–tetragonal transition temperature. Oxygen stoichiometry is, however, not a problem in the bismuth cuprates. The 124 superconductors were first prepared under high oxygen pressures. It was later found out that heating the oxide or nitrate mixture in the presence of Na_2O_2 in flowing oxygen is sufficient to obtain 124 compounds. Superconducting Pb cuprates, on the other hand, can only be prepared in presence of very little oxygen (N_2 with a small percentage of O_2). In the case of the electron superconductor, $Nd_{2-x}Ce_xCuO_4$, it is necessary to heat the material in an oxygen-deficient atmosphere; otherwise, the electron given by Ce will merely go into giving an oxygen excess material. It may be best to prepare $Nd_{2-x}Ce_xCuO_4$ by a suitable method (say decomposition of mixed oxalates or nitrates) and then reduce it with hydrogen.

6. Commonalities in the cuprates

There are many striking commonalities in the structure and properties of the high T_c cuprates. All the cuprates can be considered to be a result of the intergrowth of defect perovskite layers of $ACuO_{3-x}$ with AO-type rock-salt layers leading to the general formula $[ACuO_{3-x}]_n [AO]_{n'}$ as shown in figure 21. The 123 compounds, however, do not have rock-salt layers and may be considered as the $n' = 0$ member of this general family. The more important common features are the following:

(i) All the cuprates possess CuO_2 layers sandwiched between certain M–O layers (e.g. TlO, BiO) acting as charge reservoirs or spacers. The seat of superconductivity is in the CuO_2 layers. The T_c in Bi and Tl cuprates increases up to $n = 3$ and then decreases, the cuprate with an infinite number of Cu–O layers being an antiferomagnetic insulator (figure 22). Interaction or spacing between the Cu–O layers is crucial. This is demonstrated by recent experiments where the introduction of a fluorite layer, $[Ln_{1-x}Ce_x]_2O_2$, between two CuO_2 sheets in Bi cuprates lowers the T_c markedly (Tokura et al. 1989a). However, intercalation of iodine between the BiO layers in $Bi_2CaSr_2Cu_2O_8$ (causing a substantial increase in the c-parameter) does not affect the T_c (Xiang et al. 1990).

(ii) The Cu–O bonds in the cuprates are highly covalent.

(iii) There is an interesting comparison between the Cu–O sheets in the hole and the electron superconductors. Cuprates with the T′-structure where Cu has a square-planar coordination can be doped with electrons while those with the T-structure as in $La_{2-x}Sr_xCuO_4$ can be doped with holes (figure 20). There is an interesting symmetry between these two situations as shown in figure 23. The Cu–O–Cu angle is less than 180° in the hole superconductors while it is close to 180° in the electron superconductors. The position of the apical oxygen in the Cu–O square-pyramids or octahedra in the hole superconductors seems to modulate the width of the conduction band.

(iv) The parent cuprates in all the superconductors are antiferromagnetic insulators. For example, La_2CuO_4, $YBa_2Cu_3O_6$, $Bi_2Sr_2LnCu_2O_8$ and $Pb_2Sr_2LnCu_3O_8$ are the antiferromagnetic insulators corresponding to the superconductors $La_{2-x}Sr_xCuO_4$, $YBa_2Cu_3O_7$, $Bi_2Ca_{1-x}Ln_xSr_2Cu_2O_8$ and $Pb_2Sr_2Ca_{1-x}Ln_xCu_3O_8$ respectively. In the case of the electron superconductor $Nd_{2-x}Ce_xCuO_4$, parent Nd_2CuO_4 is the antiferromagnetic insulator.

(v) All the cuprates nominally contain mixed valent copper which can disproportionate ($Cu^{II} \rightarrow Cu^{III} + Cu^I$). In other words, the phenomenon is associated
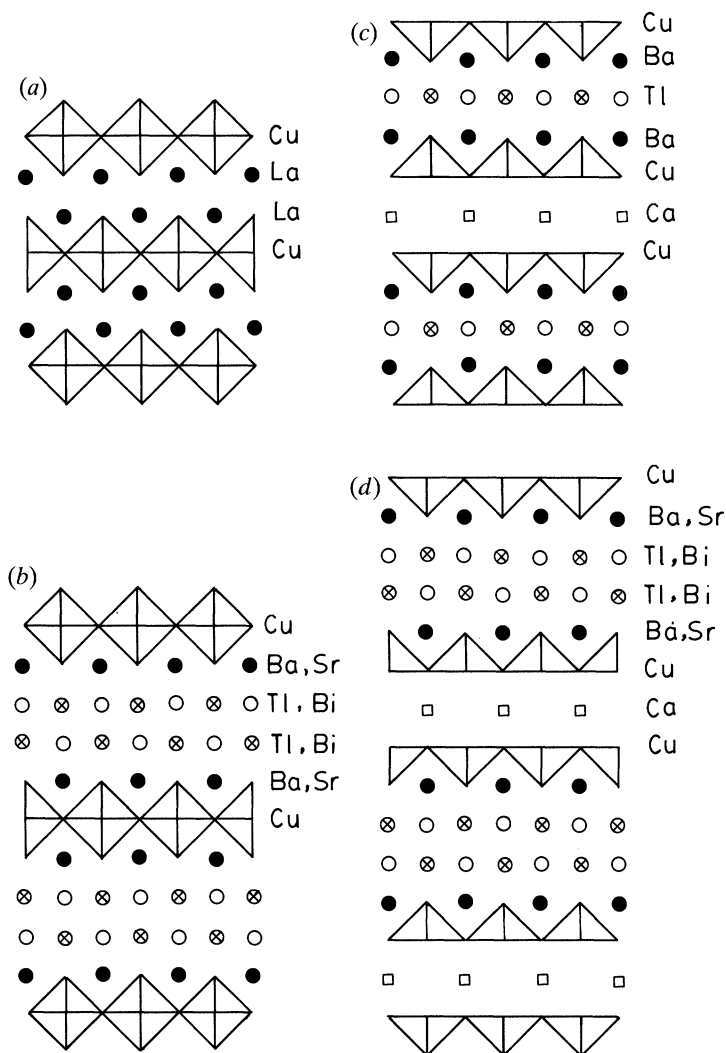
Figure 21. Schematic representation of the structures of (a) La_2CuO_4, (b) $Bi_2Sr_2CuO_6$ and $Tl_2Ba_2CuO_6$, (c) $TlCaBa_2Cu_2O_7$ and (d) $Bi_2CaSr_2Cu_2O_8$ and $Tl_2CaBa_2Cu_2O_8$. Oxygens are shown by open circles and Bi and Tl by circles with a cross. (From Rao & Raveau 1989.)
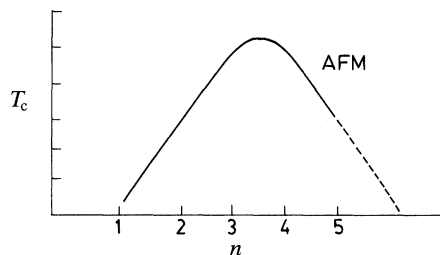
Figure 22. Variation of T_c with the number of CuO_2 sheets, n (schematic).
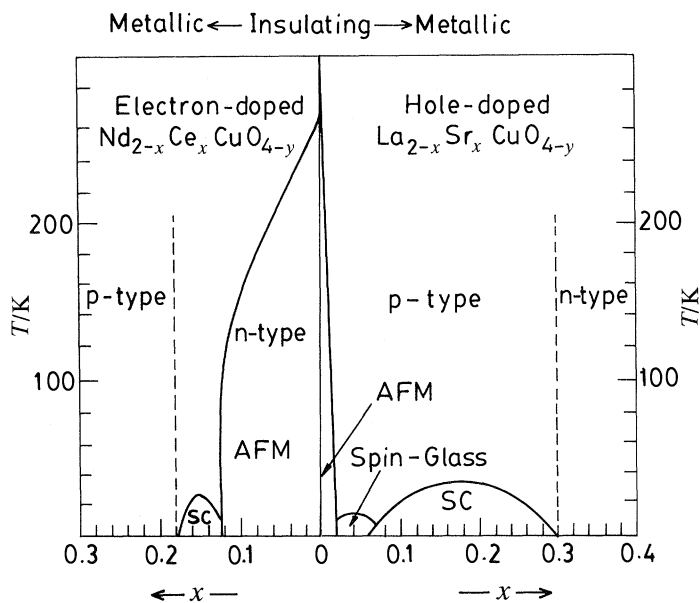
Figure 23. Symmetry in the phase diagrams of electron- and hole-superconductors, $Nd_{2-x}Ce_xCuO_4$ and $La_{2-x}Sr_xCuO_4$ (after Maple 1990.)
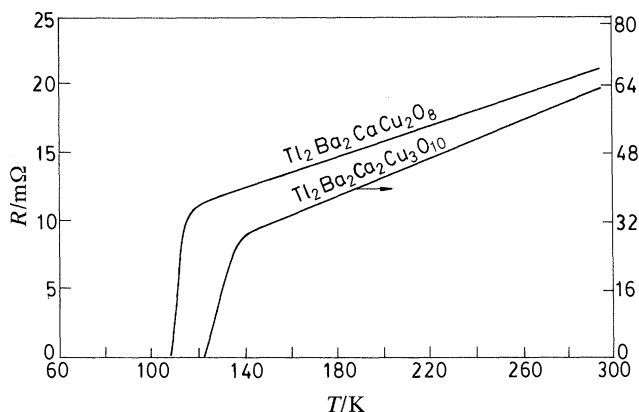
Figure 24. Linearity of the resistivity with temperature in the normal state of Tl cuprates (after Torardi *et al.* 1989).

with a band that gets filled with two electrons with stability associated with empty, half-filled and filled states.

(vi) Local charge distribution provides a basis to understand superconductivity in the cuprates. This is well demonstrated in $Pb_2Sr_2Ln_{1-x}Ca_xCu_3O_8$ where excess oxygen oxidizes Pb^{2+} and Cu^+ without affecting the CuO_2 sheets. In this system, it is necessary to replace the yttrium by calcium in between the CuO_2 sheets to render it superconducting (Cava 1990).

(vii) Oxygen stoichiometry, homogeneity and disorder play an important role in the superconductivity of the cuprates (Hewat *et al.* 1989; Rao *et al.* 1990 *d*; Raveau *et al.* 1990) as exemplified in the discussion of the various families.

(viii) All the superconducting cuprates are marginally metallic in the normal state, sitting on a metal–insulator boundary. We would, therefore, expect abnormal properties in the normal state. One of the striking abnormal normal-state properties of these materials is the linearity of resistivity over a wide range of temperatures as shown in figure 24 in the case of thallium cuprates.

7. Relation between the electronic structure and the superconductivity of cuprates

Photoemission spectroscopic studies (Allen & Olson 1990) of the high T_c cuprates show superconducting gap formation and establish that the normal state is strongly correlated with atomic spectral features at high energy. There is strong Cu(3d)–O(2p) hybridization and the E_F has nearly the same value for both hole and electron doping, lying in states filling the gap of the parent antiferromagnetic insulator. The gap filling states near E_F obey the Luttinger counting theorem.

It is important to understand the relation between the electronic structure and superconductivity of the cuprates. The problem, however, is that it is not easy to exactly describe the electronic structure of such complex oxides or to develop meaningful models to describe the properties in the superconducting and normal states. Empirical relations and chemical intuition, however, continue to be useful. Accordingly, it has been shown that the difference in the Madelung site potential between a hole on copper and one on oxygen can control their site preference and the ability to delocalize (Torrance & Metzger 1989). A relation between the oxygen content and the average [Cu–O] charge of Cu valence shows the presence of a boundary between the insulators and superconductors. The [Cu–O] charge in the sheets has been shown by an large to determine T_c (Tokura *et al.* 1988). The formal valence of Cu and O ions in the central CuO_2 planes has been calculated by de Leeuw *et al.* (1990) from experimental bond lengths following Zachariasen rules. The results show that in all the structures, the values of formal valence correlate well with the T_c; the T_c(max) increases when the holes prefer the oxygen sites over the copper sites in the CuO_2 sheets. This implies a higher value for $U - \Delta + \frac{1}{2}W$ where U is the correlation energy, Δ, the charge-transfer energy and W the band width.

In the superconducting cuprates, the correlation energy, U_{dd} within the Cu 3d manifold is considerably larger than the Cu–O charge-transfer energy, Δ, or the Cu(3d)–O(2p) hybridization strength, t_{pd}. Hybridized oxygen holes in the CuO_2 sheets are the charge carriers responsible for the superconductivity. Although many of the models for superconductivity in the cuprates consider the parent compounds to be charge-transfer gap insulators and the t_{pd} to be substantial, they do not explicitly take Δ and t_{pd} as crucial parameters. Some of the phenomenological models consider the electronic polarizability, α, to be important, but do not evaluate or relate α to Δ, t_{pd} or carrier concentration. Although it seems clear that chemical bonding factors such as Δ and t_{pd} have to be given greater attention, there has been hitherto no experimental proof to show that these are indeed as important as they appear to be. Recent Cu core-level photoemission studies of the cuprates supported by theoretical calculations have, however, changed the picture (Rao *et al.* 1990*c*, 1991*b*; Rao & Sarma 1991; Santra *et al.* 1991).

The Cu $2p_{\frac{3}{2}}$ core-level spectra of cuprate superconductors show a main feature, M, around 933 eV due to the well-screened core-hole state of $2p^5 3d^{10}$ configuration and a broad satellite, S, centred around 942 eV due to the poorly screened state of $2p^5 3d^9$
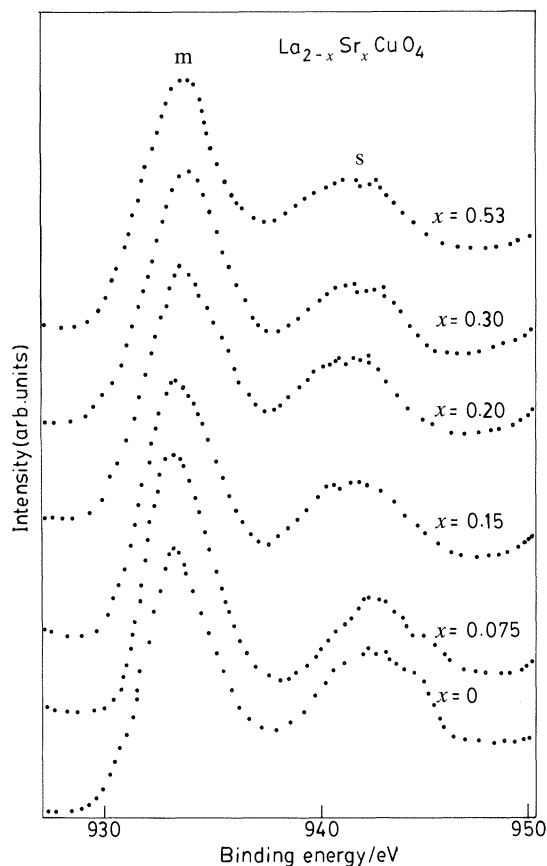
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Figure 25. Cu 2p core-level spectra of $La_{2-x}Sr_xCuO_4$.

configuration. The relative intensity of the satellite with respect to that of the main feature, I_s/I_m, is determined by the charge-transfer energy, Δ, and the Cu–O hybridization strength, t_{pd}. Making use of the I_s/I_m ratio as an experimental handle, we have investigated the role of Δ and t_{pd}. For this purpose I_s/I_m has been carefully measured in several series of cuprates with known hole concentration, n_h. To explain the nature of variation of I_s/I_m with the composition of n_h, model calculations have been carried out on a CuO_4 cluster including configuration interaction. These calculations indeed reveal how I_s/I_m depends sensitively on the Δ/t_{pd} ratio. We shall briefly examine the results of our Cu 2p core-level photoemission studies and theoretical calculations to appreciate how the Cu–O charge-transfer energy and the Cu(3d)–O(2p) hybridization strength play a crucial role in the superconductivity of the layered cuprates.

In figure 25 we show the X-ray photoemission spectra of $La_{2-x}Sr_xCuO_4$ for various values of x in the Cu $2p_{\frac{3}{2}}$ region. The spectra exhibit the well-known two-peak structure with a peak at about 933 eV (the main peak) and the other at 941 eV (the satellite) binding energies. The ratio of the satellite to the main peak intensity, I_s/I_m, in figure 25 exhibits a systematic variation with x. We have quantitatively estimated I_s/I_m as the ratio of the integrated areas under the main peak and the satellite after background subtraction of the spectra. The resulting I_s/I_m is plotted as a function of x in figure 26 for the $La_{2-x}Sr_xCuO_4$ series. In the same figure, we have also shown the

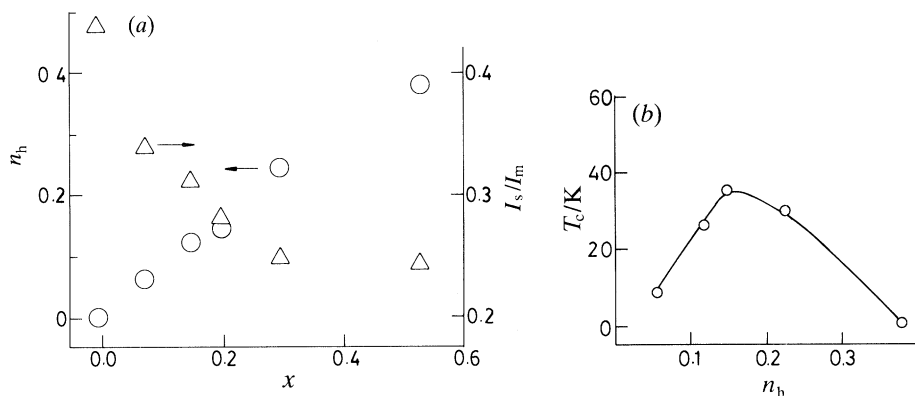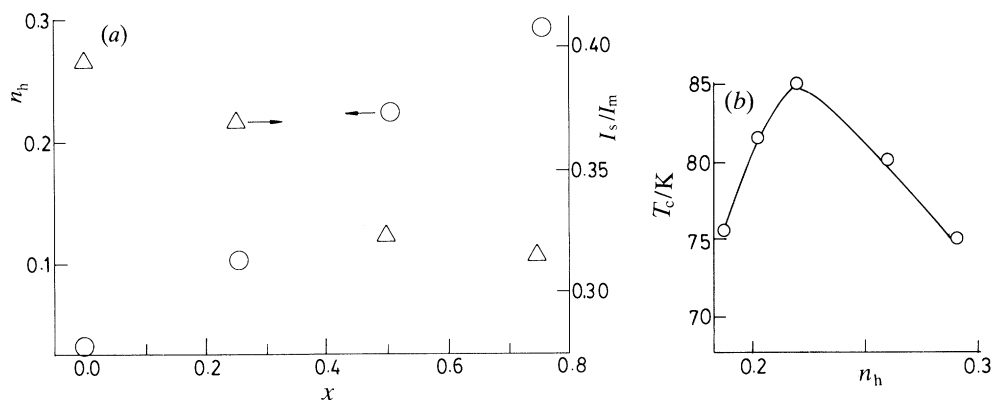Figure 26. (a) Variation of I_s/I_m and n_h with x in $La_{2-x}Sr_xCuO_4$. (b) Variation of T_c with n_h.

Figure 27. (a) Variation of I_s/I_m and n_h with x in $BiPbSr_2Y_{1-x}Ca_xCu_2O_8$. (b) Variation of T_c with n_h.

dependence of the experimentally obtained (by iodometric titrations) hole concentration, n_h, on x in these compounds. The inset shows the variation of the superconducting transition temperature T_c on n_h. This system traverses through the insulator–superconductor–metal régimes with increase in x. The I_s/I_m decreases continuously though these régimes, while n_h increases.

This behaviour seems to be common to all the series of superconducting cuprates that we have investigated. In figure 27 we plot the variation of I_s/I_m and n_h with x in the $BiPbSr_2Y_{1-x}Ca_xCu_2O_8$ series. We also show the variation of T_c with n_h in this series in figure 27b. The T_c reaches a maximum of about 85 K around $n_h = 0.22$; n_h once again exhibits a linear dependence on x with a slope of less than unity, while I_s/I_m monotonically decreases with x.

We show the dependence of n_h and I_s/I_m on x in the $Bi_2Ca_{1-x}Ln_xSr_2Cu_2O_8$ (Ln = Y or rare earth) series of compounds in figure 28. The inset shows the variation of T_c with n_h in this series. The T_c appears to exhibit a broad maximum at about $n_h = 0.2$ in these compounds. Interestingly in this series, we obtain a non-monotonic dependence of n_h on x. The n_h increases with x for small values of x up to about 0.25 and then decreases continuously up to $x = 1.0$. This is in contrast to the dependence of n_h on x in the other two series shown in figures 26 and 27. It is significant that in this series, I_s/I_m also exhibits a non-monotonic behaviour, showing a decrease up to
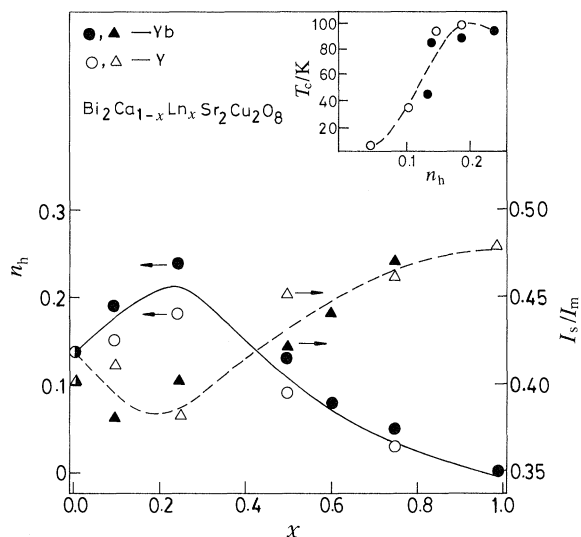
C. N. R. Rao

Figure 28. Variation of I_s/I_m and n_h with x in $Bi_2Ca_{1-x}Ln_xSr_2Cu_2O_8$.
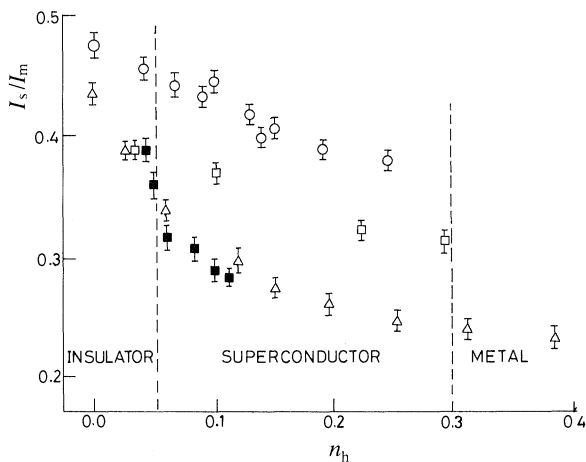
Figure 29. Variation of I_s/I_m with n_h. $\blacksquare$, $BiPbSr_{1+x}Pr_{1-x}CuO_6$; $\diamond$, $Bi_2Ca_{1-x}Ln_xSr_2Cu_2O_8$
(Ln, rare earth); $\triangle$, $La_{2-x}Sr_xCuO_4$; $\square$, $Bi_2PbSr_2Y_{1-x}Ca_xCu_2O_8$.

$x = 0.2$ and then a monotonic increase up to $x = 1.0$. This provides a crucial test of
the fact that I_s/I_m appears to have the complimentary dependence on x compared
with n_h. This implies that I_s/I_m will monotonically decrease in all the series with
increasing n_h.

  There is a relation between the experimentally obtained I_s/I_m and n_h values as
shown in figure 29 where we have plotted the I_s/I_m ratios against the n_h values for
the three series, $La_{2-x}Sr_xCuO_4$, $BiPbSr_2Y_{1-x}Ca_xCu_2O_8$ and $Bi_2Ca_{1-x}Ln_xSr_2Cu_2O_8$
(Ln = Y or Yb) as well as for the series, $BiPbSr_{1+x}Pr_{1-x}CuO_6$. It becomes
absolutely clear from this figure that in each of the three series, I_s/I_m decreases
monotonically with increased hole doping. The $La_{2-x}Sr_xCuO_4$ and the BiPb
$Sr_{1+x}Pr_{1+x}CuO_6$ series exhibit the most pronounced dependence of I_s/I_m on n_h (over
a narrow range of n_h), while the $Bi_2Ca_{1-x}Ln_xSr_2Cu_2O_8$ and $Bi_2PbSr_2Y_{1-x}Ca_xCu_2O_8$
series have a weaker dependence on n_h. In figure 29 we have also marked the
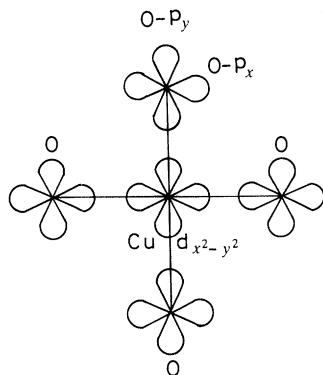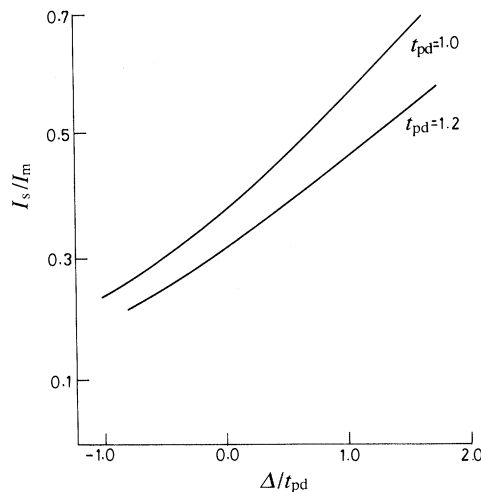
Figure 31

Figure 30

Figure 30. Bonding in a CuO_4 unit.

Figure 31. Variation of I_s/I_m with Δ/t_{pd}.

insulating, superconducting and metallic regions of the cuprates as n_h is varied by chemical doping to demonstrate how I_s/I_m varies continuously through these different régimes.

To understand the variation of I_s/I_m in the cuprates, we have performed model calculations of the Cu $2p_{\frac{3}{2}}$ core level photoemission spectral features (Rao *et al.* 1991 *b*; Rao & Sarma 1991; Santra *et al.* 1991). For this purpose, we consider a CuO_4 cluster as shown in figure 30. We include the Cu $3d_{x^2-y^2}$ and the oxygen in-plane $2p_x$, $2p_y$ orbitals. In the D_{4h} symmetry of the CuO_4 cluster, the Cu $3d_{x^2-y^2}$ orbital transforms according to the b_{1g} irreducible representation. Out of the eight oxygen $2p_{x,y}$ orbitals shown in the figure, only one linear combination of these (namely $p_x^1 - p_y^2 - p_x^3 + p_y^4$) has the right symmetry (b_{1g}) to mix with the $3d_{x^2-y^2}$ orbital of Cu. Within this approximation the hybridization of the various oxygen orbitals do not play any important role as far as the spectral features are concerned, since these hybridization interactions will merely shift the b_{1g} combination of the O $2p$ orbitals in energy and renormalize the charge-transfer excitation energy (Sarma & Ovchinnikov 1990). We consider only one hole per Cu, so that the Coulomb interaction strengths, U_{dd}, U_{pp} and U_{pd} do not play any role. Thus, the spectral features depend only on the charge-transfer energy, Δ, between the Cu $3d_{x^2-y^2}$ and the oxygen-derived b_{1g} orbitals, the hybridization interaction strength, t, between the $3d$ and ligand b_{1g} level, and the $2p$ core-hole–$3d$-hole Coulomb repulsion, U. This problem can be exactly solved within the sudden approximation for the spectral features (Rao & Sarma 1991). In all our calculations we fix the value of the Coulomb repulsion, U, between the Cu $2p$-core hole in the Cu $3d$ valence-hole at 8.0 eV.

In figure 31, we show the variation of the calculated I_s/I_m with Δ/t_{pd}, where $t_{pd} = \frac{1}{2}t$ is the hybridization strength between the Cu $3d$ and the O $2p$ orbitals for two different values of t_{pd}. We find from this figure that I_s/I_m increases with increasing Δ/t_{pd}. At large values of t_{pd}, the variation of I_s/I_m with Δ/t_{pd} becomes less pronounced; the dependence of I_s/I_m on Δ appears to be more pronounced when t_{pd} is small. In this context, we note that the experimental I_s/I_m values for $La_{2-x}Sr_xCuO_4$

Figure 32

Figure 33

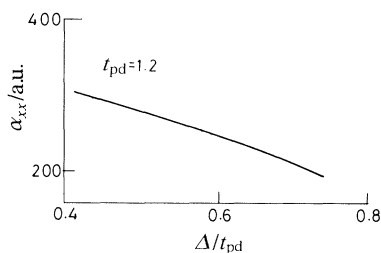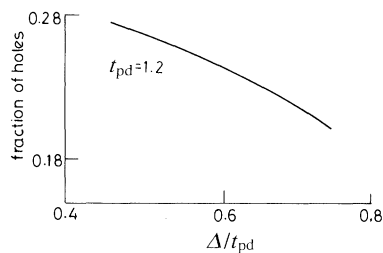Figure 32. Variation of the polarizability of the CuO$_2$ sheets, α_{xx}, with Δ/t_{pd} (from Rao *et al.* 1991).

Figure 33. Variation of the fraction of holes with Δ/t_{pd} (from Rao *et al.* 1991).

and BiPbSr$_{1-x}$Pr$_{1+x}$CuO$_6$ show a marked variation with n_h and x, while I_s/I_m for Bi$_2$Ca$_{1-x}$Ln$_x$Sr$_2$Cu$_2$O$_8$ and Bi$_2$PbSr$_2$Y$_{1-x}$Ca$_x$Cu$_2$O$_8$ exhibit a less pronounced variation. It, therefore, appears that the decrease in I_s/I_m with x or n_h observed in these series of cuprates as well as the slopes of these variations are related to the magnitude of Δ/t_{pd}.

Our calculations of I_s/I_m in the cuprates indicate that the decrease in the charge-transfer energy is primarily responsible for the variation of the Cu 2p satellite intensity with increasing n_h. This is not an unreasonable expectation since increasing n_h tends to renormalize the charge-transfer energy to smaller values in the presence of a finite interatomic Coulomb interaction strength (U_{pd}). Since we do not explicitly take into account U_{dd} in our model, the renormalized Δ value should appear to be decreasing with increasing n_h. An earlier model (Sarma & Taraphder 1989) that includes U_{pd} interactions explicitly has indeed shown that the I_s/I_m is expected to decrease on hole-doping (increasing n_h) primarily due to the renormalization of Δ to a smaller value.

The T_c in the various families of cuprates generally show a maximum at a certain n_h value (figure 18). Accordingly, at a given n_h-value where the T_c is maximum (say $n_h \approx 0.15$), increasing I_s/I_m (going vertically in figure 29) is accompanied by an increase in T_c. Thus, Bi$_2$Ca$_{1-x}$Ln$_x$Sr$_2$Cu$_2$O$_8$ exhibits the highest T_c of around 100 K, while La$_{2-x}$Sr$_x$CuO$_4$ is associated with the lowest T_c; BiPbSr$_2$Y$_{1-x}$Ca$_x$Cu$_2$O$_8$ falls in between, YBa$_2$Cu$_3$O$_7$ ($n_h = 0.2$ at maximum T_c of *ca.* 90 K) shows an I_s/I_m value (0.45) close to that of Bi$_2$Ca$_{1-x}$Ln$_x$Sr$_2$Cu$_2$O$_8$. As we have already shown, an increase in the I_s/I_m ratio is associated with an increase in Δ/t_{pd} (figure 31) which can arise from either a decrease in the t_{pd} value or an increase in the Δ value. It therefore appears that T_c in the different series of the cuprates are tuned by changing the value of Δ/t_{pd} *via* a change in the hole-doping level.

We show in figure 32 the static electronic polarizability, α_{xx}, calculated (Rao *et al.* 1991*b*) for a Cu$_4$O$_8$ cluster as a function of Δ/t_{pd}, while we show the fraction of the oxygen holes in the ground state wave function as a function of Δ/t_{pd} in figure 33. We find that α is rather large compared with the value for a single-band Hubbard model at $U = 4t$ of a similar size system at half-filling. The large static polarizability indicates a large dynamic polarizability as well, which would favour hole pairing in these systems. The polarizability increases with decreasing Δ/t_{pd}, concomitant with the decrease of the I_s/I_m ratio with decreasing Δ/t_{pd}. At the same time, there is an increase in the weightage of the fraction of oxygen holes in the ground state wave function.
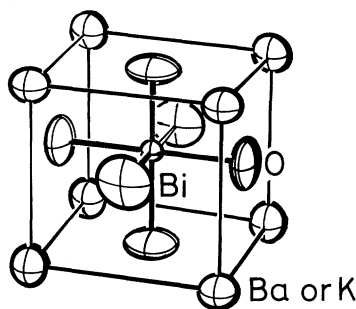
Figure 34. Structure of $Ba_{1-x}K_xBiO_3$.

Our studies of the Cu(2p) photoemission in cuprates combined with theoretical calculations enable us to come to the following conclusions.

(i) The intensity of the Cu 2p satellite, relative to the main feature, I_s/I_m, in the core-level spectra of the cuprates provides an experimental handle to investigate the role of important chemical bonding factors such as the Cu–O charge-transfer energy, Δ, and the Cu(3d)–O(2p) hybridization strength, t_{pd}.

(ii) The I_s/I_m ratio varies continuously with composition through the insulator–superconductor–metal régimes in the various series of cuprates. The experimental hole concentration n_h and I_s/I_m vary in opposite directions with composition suggesting that these two quantities are inversely related.

(iii) Theoretical calculations show that I_s/I_m increases monotonically with increasing Δ/t_{pd}. A relatively small Δ/t_{pd} gives rise to a large n_h (and small I_s/I_m). The value of n_h itself is nearly the same at maximum T_c in all the cuprate superconductors containing the same number of CuO_2 sheets.

(iv) At small Δ/t_{pd} values, the electronic polarizability, α, of the CuO_2 sheets will be large, favouring hole-pairing; α increases with increasing n_h or decreasing Δ/t_{pd}. Furthermore, Bose condensation of such pairs would be favoured by the two dimensionality of the CuO_2 sheets.

(v) Since all the cuprates containing the same number of CuO_2 sheets have roughly the same n_h values at maximum T_c, it appears that they will also be associated with similar, low Δ/t_{pd} and high α values.

8. Copper-free oxide superconductors

Historically, the two oxide systems not containing copper which showed relatively high T_cs in the range of 13 K are $BaBi_{1-x}Pb_xO_3$ (Sleight *et al.* 1975) and $Li_{1+x}Ti_{2-x}O_4$ (Johnston *et al.* 1973). Both these oxides have mixed valent cations. In the bismuthate system, which has the perovskite structure, the nominal Bi^{IV} disproportionates into Bi^{III} and Bi^V in the insulting phase ($x < 0.75$); in other words, there is a charge-density-wave (CDW) gap. There is a sharp insulator-metal transition at $x = 0.75$, when the CDW gap disappears and superconductivity manifests itself; Bi^{IV} ions are delocalized in the metallic/superconducting phase (Kulkarni *et al.* 1990). In superconducting $Ba_{1-x}K_xBiO_3$ (figure 34) with a T_c of *ca.* 30 K (Cava *et al.* 1988a), introduction of mixed valency by substitution of Ba by K competes with the CDW. These bismuthates are considered to be negative U cases with $\Delta \gg U$. Although some of the features of bismuthates are similar to those of the cuprates, they show some properties which are quite different (Hinks 1990). Thus $Ba_{1-x}K_xBiO_3$ shows a

large ^{18}O isotope effect (unlike the two-dimensional cuprates), but no static magnetic order. $Ba_{1-x}K_xBiO_3$ appears to be a superconductor in the weak to moderate coupling limit and the high T_c is due to a large electron–phonon coupling constant. The mechanism of superconductivity in these materials seems to be different from that of cuprates. Other than $Ba_{1-x}K_xBiO_3$, there has not been much success in synthesizing three-dimensional oxides with high T_cs (see, for example, Nagarajan *et al.* 1991).

Among the other copper-free oxide superconductors, the lanthanum nickelates were suspected to show superconductivity because of the diamagnetic behaviour found in some samples of $La_{2-x}Sr_xNiO_4$ and related compounds (Nanjundaswamy *et al.* 1990). It has, however, not been possible to reproduce these findings universally and the origin of diamagnetism observed in some of the samples is not clear (Sreedhar & Rao 1990). Hopes were raised by a recent Japanese report of T_cs near 200 K in the Tl–Sr–V–O system, but we have found that these results are not reproducible. There was a Russian report that $LaCa_2Co_3O_y$ was superconducting with a T_c of around 227 K, but we have not been able to reproduce this result as well. Clearly there must be other interesting oxides without copper which should exhibit high T_cs. Future investigations may bring into light such metal oxides.

9. Chemical applications

Potential applications of superconducting cuprates in electronics and other technologies are commonly known. These cuprates also exhibit significant catalytic activity. Thus, $YBa_2Cu_3O_{7-\delta}$ and related cuprates act as catalysts in oxidation or dehydrogenation reactions (Hansen *et al.* 1988; Halasz 1989; Mizuno *et al.* 1988). Carbon monoxide and alcohol are readily oxidized over the cuprates. NH_3 is oxidized to N_2 and H_2O on these surfaces. Ammoxidation of toluene to benzonitrile has been found to occur on $YBa_2Cu_3O_7$ (Hansen *et al.* 1990).

The catalytic activity of the cuprate superconductors prompted us to examine their possible use as gas sensors. It should be noted that a good gas sensor would require not only the catalytic property of the oxide surface but also high sensitivity. For example, the electrical resistivity of the material should change sharply on contact with the gas or vapour in question. The superconducting compositions of the cuprates being metallic in the normal state, would therefore not be best suited for sensing while they may be good catalysts. With suitable compositional variation wherein the resistivity of the material is increased in order to have the right régime for sensing, it is possible to effectively use these materials. We have indeed found $La_{2-x}Sr_xCuO_4$ ($0 < x < 0.2$) and $Bi_2Ca_{1-x}Y_xSr_2Cu_2O_{8+\delta}$ ($x > 0.5$) are good sensors for alcohol and other vapours; the superconducting compositions are not. In figure 35, we show some of the recent results obtained by Grantscharova and Raju in this laboratory. We see that these materials are good sensors for alcohol and ether. Further studies on the gas sensor characteristics of superconducting materials would be worthwhile.

10. Concluding remarks

Structure–property relations and other aspects of the oxide superconductors that I have described so far should clearly indicate how chemistry becomes important in not only synthesizing novel materials of desired structures and properties, but also in understanding the phenomenon of high-temperature superconductivity. Our
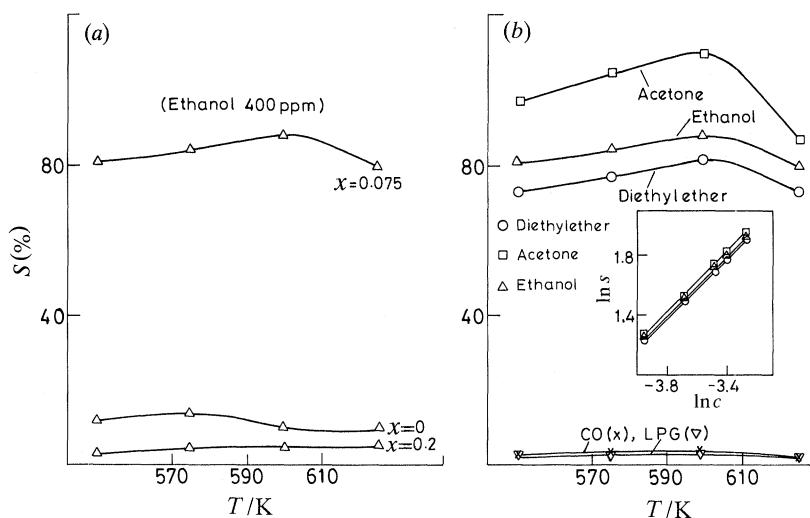
Figure 35. Gas sensing ability of $La_{2-x}Sr_xCuO_4$ (S is sensitivity). Inset shows log sensitivity against log concentration plot (unpublished results of Grantscharova, Raju and Rao).

search for newer and better high T_c materials is far from over. We are yet to investigate many other oxide and related systems, besides improving on the already known ones. Some of the important objectives of research in superconductivity today would be the following.

(i) To acquire better and more experimental data on the known high T_c materials in order to improve our understanding of the properties.

(ii) To develop suitable models to understand the mechanism responsible for high T_c superconductivity and carry out those experiments which would clearly delineate the various factors responsible for superconductivity.

(iii) To search for new materials exhibiting high T_c and especially those not containing Cu (since most of present models require the d orbitals of Cu).

(iv) To improve our understanding of the chemistry of materials processing as well as the ceramic properties of the oxide superconductors.

(v) To prepare high quality films, tapes, wires, etc. with desired J_c and other properties for applications.

(vi) To investigate catalytic, gas-sensing and other chemical applications, besides the well-known applications in electronics and other areas.

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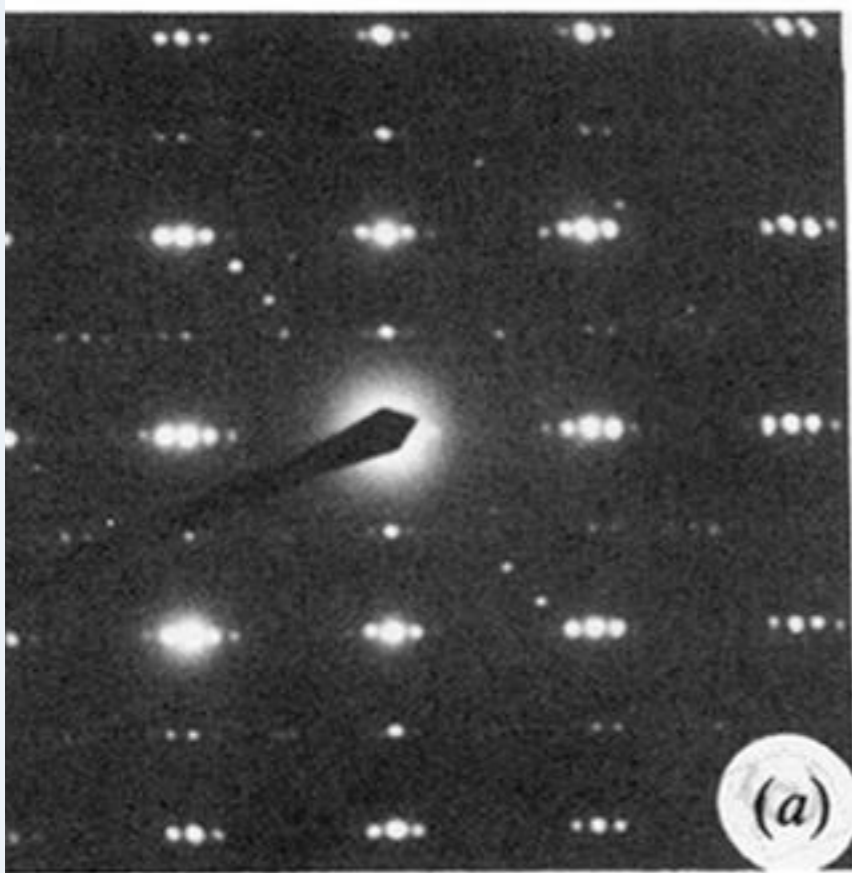Allen, J. W. & Olson, C. G. 1990 *MRS Bull.* **15**, 34, and the references cited therein.

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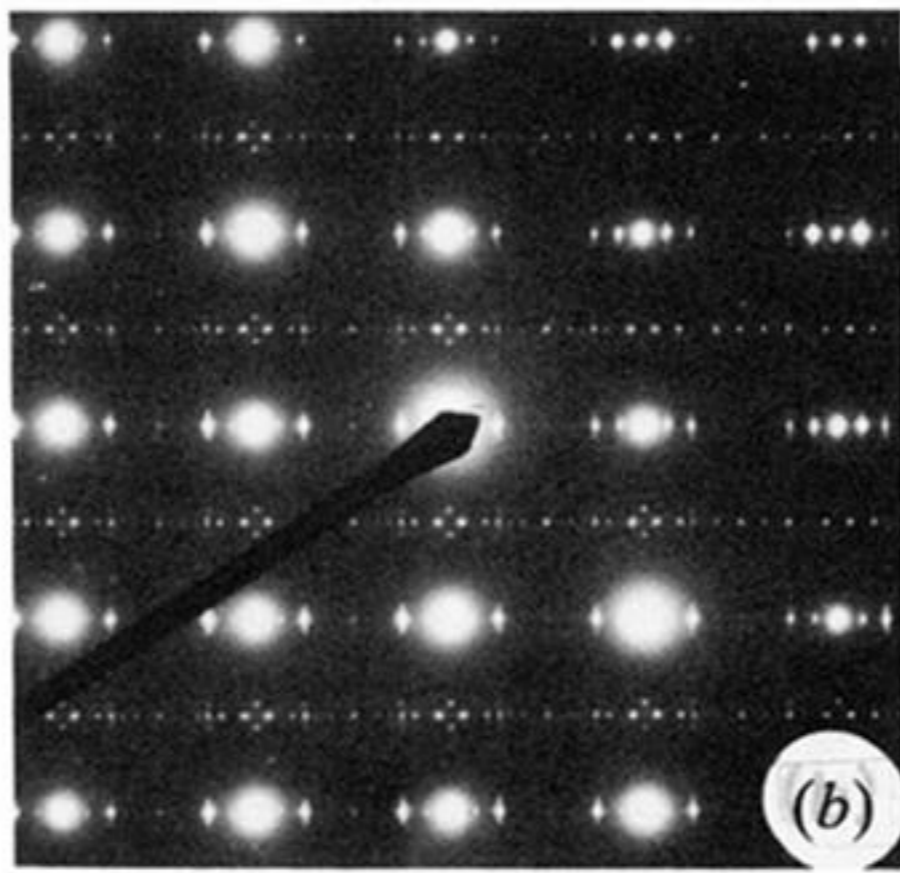
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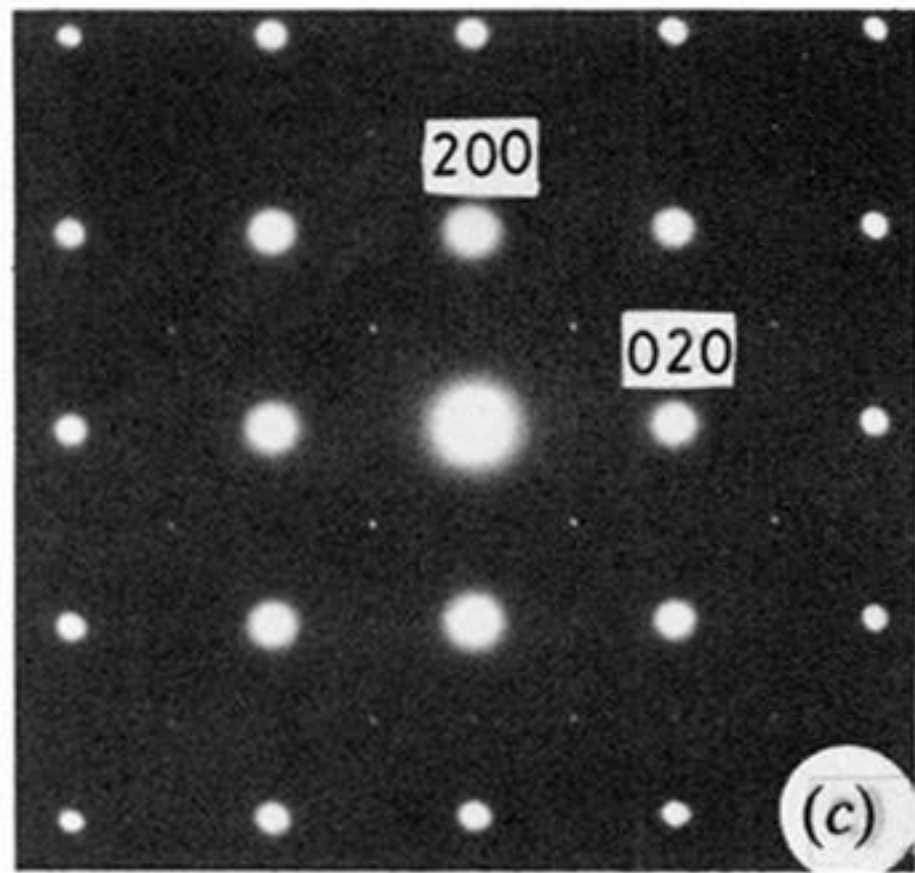
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Figure 5. (a) Bright field electron microscopic images of twins in $YBa_2Cu_3O_7$. The splitting of the {110} Brugg spots is clearly seen in SAED pattern given in the inset. (b) 90° twins in $YBa_2Cu_3O_7$.

Figure 11. Electron diffraction patterns showing (a) superlattice modulation in superconducting $Bi_2CaSr_2Cu_2O_8$ recorded along the (001) direction, (b) superlattice modulation in non-superconducting $Bi_2YSr_2Cu_2O_8$, and (c) absence of superlattice modulation in superconducting $BiPbSr_2Y_{0.5}Ca_{0.5}Cu_2O_8$.